29 September 1961

To: C. L. Johnson

Subject: OZONE

Accompanying this memorandum is the latest report made by our senior physicist on the distribution and physical chemistry on the ozone which we feel can be expected during operational conditions.

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I believe that [redacted] report very aptly explains the situation. To compile the data contained in this document, visits were made to a number of high altitude research laboratories and government facilities, including the Aerophysics Laboratory in Hanscom Field, Mass.

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[redacted] makes the recommendation that some actual erosion measurements be made, probably in a high speed wind tunnel. We will await your advice or opinion before proceeding with such tests or continuing our background research into the subject of ozone attack on organic materials.

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29 September 1961

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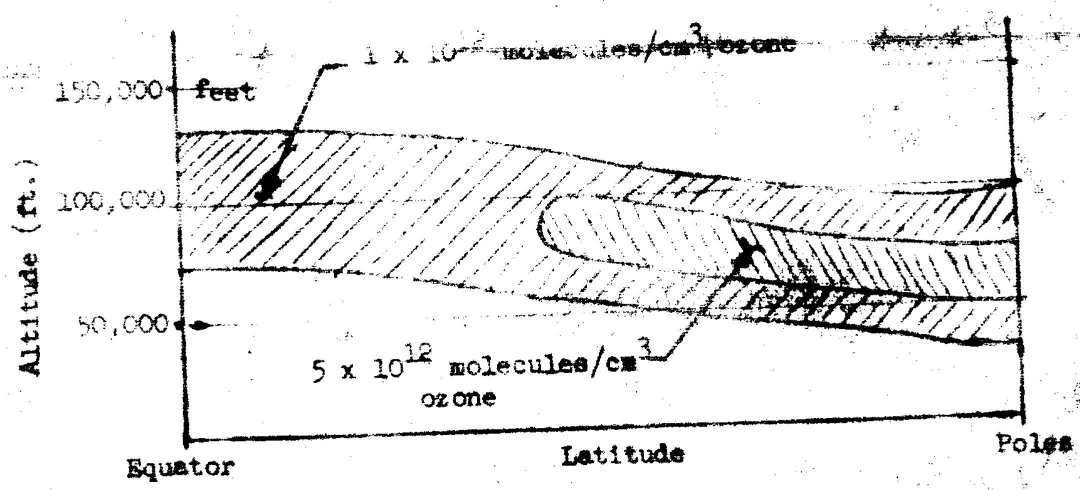
Memo To: [redacted]

From

Subject: DISTRIBUTION AND PHYSICAL CHEMISTRY OF OZONE

1. Distribution of Ozone in the Atmosphere

According to the best current estimates of meteorologists, the average distribution of ozone is quite concisely depicted by the following chart:



The isopleths shown are of constant concentration.

The rest of the facts that have been obtained during our studies on ozone distribution may be reported in the following series of isolated statements:

a. The ozone layer rises and falls with the tropopause and is denser when the tropopause is low (the above chart is an example of this).

b. The theoretical maximum density (calculated from the physical chemistry and optical absorption of the atmosphere) is 10×10^{12} molecules of ozone per cm^3. This is the value that was assumed in my previous memo on this subject of 14 July 1961.

c. The compression of the stratosphere in the lee of moving cyclones increases the ozone density. It is not believed that this concentration would exceed 10×10^{12} molecules/cm^3, but accurate observational data is extremely scanty as the thick clouds attending such conditions preclude the use of the more convenient methods of ozone measurement.

d. The threshold of sensitivity for the olfactory detection of ozone was stated to be 1/2 part per million at normal temperature and pressure. This corresponds to 14×10^{12} molecules/cm^3. Thus, if the odor of ozone is detectable, we may conclude that it is present in higher concentrations than will ever be encountered in the atmosphere.

As a result of these studies, it may be logically assumed that an average ozone concentration of 5×10^{12} molecules/cm^3 at 80,000 ft will be encountered during missions of the type considered. An assumption of a maximum of 10×10^{12} would include an adequate margin of safety.

2. Physical Chemistry of the $O_3 - O - O_2$ System

The physical chemical quantities of interest are listed as follows with the energy units in small calories (R = gas constant, T = absolute temperature in °K, and M = third body molecules):

REACTION	EQUILIBRIUM CONSTANT	HEAT OF REACTION	RATE CONSTANT
1) $O + O_3 \rightarrow 2O_2$	$0.23 \exp\left(\frac{-92,000}{RT}\right)$		$3.0 \times 10^{13} \exp\left(\frac{-6000}{RT}\right)$ $sec^{-1}\ mol^{-1}\ cc$
2) $O_3 \rightarrow O_2 + O$	$77 \exp\left(\frac{-24,600}{RT}\right)$ mol/cc	24,000	
3) $O_2 \rightarrow O + O$		117,000	
4) $O + O + M \rightarrow O_2 + M$			$9.8 \times 10^{14}\ sec^{-1}\ mol^{-2}\ cc^2$ at 300°K
5) $O + O_2 + M \rightarrow O_3 + M$			$1 \times 10^{14}\ sec^{-1}\ mol^{-2}\ cc^2$ Temperature independent
6) $O_3 + M \rightarrow O + O_2 + M$			$4.6 \times 10^{15} \exp\left(\frac{-24,600}{RT}\right)$ $sec^{-1}\ mol^{-1}\ cc$

This data may be applied to two different situations:

a. Vehicle skin areas where the gas is assumed to be at pressure equilibrium with the surrounding atmosphere at an altitude of 80,000 feet and aerodynamically heated to a temperature of 550°C (562°K). Ambient temperature and pressure are assumed to be that of the standard atmosphere (28 mb and 216°K).

b. Leading edge conditions. Here, pressure equilibrium can again be assumed because shock compression under the proposed flight conditions is quite small (20%). Gas temperature should be close to the stagnation temperature of a Mach 3.2 flow which is assumed to be 800°F (697°K).

The equilibrium concentrations of O and O_3 were calculated from the above constants and were found to be completely negligible. The ratio of concentration of O to O_3 is of interest. This is 0.17 at 550°F and 16 at 800°F. This means that, at equilibrium, 17% of the ozone is decomposed at the lower temperature but almost completely converted to O at the leading edges. In the surrounding 216°K atmosphere, the ratio is 10^{-16}, producing virtually no decomposition of ozone.

The concentration of the various species in molecules/cm^3 under the two conditions listed above is shown in the following table, where it is assumed that ozone is present at a concentration of 10^{13} in the ambient atmosphere and no reaction of the ozone is taking place:

SPECIES	CONDITIONS a	CONDITIONS b
O_2	5.9×10^{16}	4.7×10^{16}
O_3	3.9×10^{12}	3.1×10^{12}
N_2	23×10^{16}	19×10^{16}

The reaction rates under the above conditions may be discussed through the use of the previously listed rate constants. Under Condition (a), Reactions (5) and (6) establish a pseudo-equilibrium condition in about a tenth of a second in which the O concentration is approximately one-third of the O_3 concentration. These then disappear together by Reaction (1). Reaction (4), involving a three body collision, two of which are O atoms, has a negligible rate for all situations considered.

The following tabulation summarizes the results of these reaction rate calculations for Condition (a).

TIME (sec.)	O_3 CONCENTRATION molecules/cm^3	O CONCENTRATION molecules/cm^3
0	3.9×10^{12}	0
.1	2.6	$.8 \times 10^{12}$
1	2.2	.7
10	1.0	.3
100	.15	.05

From the above it may be concluded that the active oxygen concentration in an than a minute.

Under Condition (b), the rate of Reaction (6) far exceeds that of (5) and (1) so that all of the ozone is converted to atomic oxygen in 40 micro seconds. Therefore, one may assume at atomic oxygen concentration of about 3×10^{12} molecules/cm^3 at the leading edge.

If a parcel of gas has passed the 800°F leading edge region and has been cooled to the predicted skin temperature of 550°F, reconversion of atomic oxygen to ozone will begin. However, this requires a time interval in the order of a tenth of a second, which is much longer than flow times over aerodynamic surfaces at a Mach number of 3. Consequently, it is inferred that all such surfaces are subject to the same concentration of atomic oxygen.

3. Conclusions

After analysis of the above considerations, we may assume that with an adequate margin of safety, the concentration of active oxygen is less than 4×10^{12} molecules/cm^3. Erosion to an organic material from this amount of atomic oxygen would be at the maximum about .001 inch per hour, and with excellent chance that the rate would be considerably less.

Interior portions of the vehicle subject to soak temperatures of 550°F would probably not experience any appreciable deterioration since this temperature suffices to effect the decomposition of ozone to molecular oxygen in about a minute.

Exterior surfaces, however, may be expected to be in an environment containing up to 4×10^{12} molecules/cm^3 of atomic oxygen. This is considerably more serious condition than that which would be experienced if the active oxygen were in the form of ozone. Not only is atomic oxygen more reactive than ozone, but it is so small a molecule that it could readily diffuse through protective oxide layers and attack material beneath them.

It is recommended that any meaningful tests on materials should reproduce the above conditions. Merely generating the indicated concentration of ozone would not be sufficient. Appropriate conditions could be realized by placing an ozone generator (which actually produces atomic oxygen) in a hot gas flow a short distance upstream from the test object.

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